

Thermal Expansion of Surface-Frozen Monolayers of Semifluorinated Alkanes

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The linear coefficient of thermal expansion of a quasi-2D surface-frozen crystalline layer is measured, using surface X-ray diffraction, for three different semifluorinated alkane diblocks. The values obtained are in good agreement with those of surface-frozen monolayers of fully protonated alkanes. An unexpected strong dependence on the protonated block's length is found and discussed.

I. Introduction

Surface freezing (SF), the formation of an ordered monolayer on the surface of a melt a few degrees above the bulk solidification temperature, was discovered to occur in several families of chain molecules,^{1–3} e.g., alkanes,⁴ alcohols,^{5,6} alkenes,⁷ etc. While for normal-alkanes the existing theoretical model provides a reasonable quantitative description of the effect,^{8–11} significant deviations between theory and experiment exist in some derivative molecules.¹²

Semifluorinated alkanes (SFA), $F(CF_2)_m(CH_2)_nH$ (abbreviated as F_mH_n), are molecules that, as normal alkanes, possess only pure van der Waals (vdW) interactions. However, the molecule's diblock structure and the mutual phobicity of the fluorinated and hydrogenated parts^{13,14} break the inversion symmetry of these molecules. This symmetry breaking is further enhanced by the different structure of the two blocks, a planar zigzag for the H block and a helical one for the F block, and their different rigidities and cross-sectional areas, both significantly larger for the F block. SFAs allow varying the relative strength of the interactions by using different molecular lengths, $m + n$, and block size ratios, n/m . These molecules were shown^{12,15} to exhibit SF over a range of block lengths n and m . While the temperature range of existence of the surface frozen phase in normal alkanes is smaller than ~ 3 °C, some of the SFAs show significantly broader ranges of surface freezing,¹⁶ thus permitting the measurement of

the thermal expansion of the quasi-2D surface-frozen crystal over a significant temperature range. Two different phases were reported^{12,15} to exist for the SFA: the low n/m molecules exhibit a reversible first-order surface transition to an hexagonally packed monolayer, while the high n/m ones form an in-plane disordered layer, which melts by a second-order-like continuous transition. Herein we are concerned solely with the low n/m species. The surface-frozen layer consists, in this case, of a monolayer of surface-normal SFA molecules, the F blocks of which point into the vapor, while its H blocks extend loosely into the bulk. We note in passing that a more elaborate structure where the SF layer is a bilayer with a 20–30% coverage in the lower monolayer was found to be consistent as well with experiment.^{12,15} In both models the surface-normal-oriented F blocks reside at the free surface of the sample. Since the average cross-sectional area of the F block is ~ 28 Å²,^{17,18} as compared to only ~ 19 Å² for a normal-alkyl chain,¹⁹ the close-packed ordering observed in the SF layer implies that the order is dominated by the larger F-block's cross-sectional area. Thus one would expect that the F blocks dominate the structural properties of the SF monolayer and, in particular, the thermal expansion. Moreover, the cross section of the very rigid, helical F block is independent of the F block length. Thus, no variations are expected in the expansion coefficient upon varying n or m in these materials. Contrary to these expectations, the present study demonstrates a pronounced dependence of the structure and possibly also the thermal expansion, on the length n of the H block and on n/m . Possible reasons for this dependence are presented and discussed.

II. Experiment

A. Samples. The samples (F_8H_8 , $F_{10}H_8$, and $F_{10}H_6$) were synthesized by reacting $F(CF_2)_mI$ with $CH_2=(CH_2)_{n-1}H$ and reducing the product with tributyl tin hydride to remove the iodine.^{20,21} The purity of the samples was $>96\%$ and $>99\%$ for $F_{10}H_6$ and for $F_{10}H_8$, respectively, and unknown, but similar, for F_8H_8 .

B. Measurements. The surface structure was studied using surface-specific X-ray techniques, which have been described

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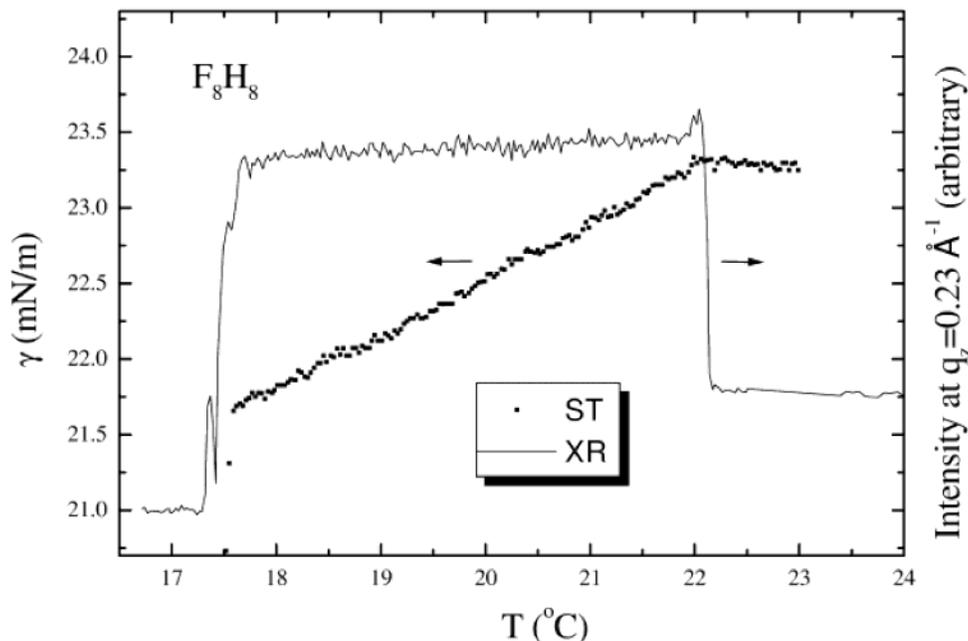


Figure 1. Temperature variation of the surface tension, γ (points), and X-ray reflectivity (line) at a fixed surface-normal momentum transfer $q_z = 0.23 \text{ \AA}^{-1}$ for F_8H_8 . Note the sharp breaks observed at the formation of the surface monolayer, $T_s \approx 22 \text{ }^\circ\text{C}$, and at bulk freezing, $T_f \approx 17.5 \text{ }^\circ\text{C}$.

previously in detail in the literature.^{4,22} Only a brief summary will be given here, concentrating mostly on features peculiar to this study.

The X-ray measurements were carried out at the Harvard/BNL liquid surface diffractometer on beamline X22B, National Synchrotron Light Source, Brookhaven National Laboratory, using X-rays of wavelength 1.57 \AA . The cell structure and other details were reported earlier.²³ The surface-normal density profile was explored by X-ray reflectivity (XR) to determine the SF layer thickness and ensure its overall quasi-2D nature.²⁴ Grazing incidence diffraction (GID) was used to study the in-plane structure of the SF layer. Bragg rod (BR) measurements^{24,25} were carried out to ensure that the GID pattern observed originates in the quasi-2D surface-frozen layer and not in small 3D crystallites, which may reside at the surface. Temperature-dependent surface tension (ST) measurements were also carried out to detect the surface-frozen phase, ascertain that indeed the low n/m phase is observed, and determine the temperature range of SF of each compound.

III. Results

The XR and ST measurements¹⁶ showed that the surface layer of F_8H_8 , $F_{10}H_8$, and $F_{10}H_6$ crystallizes at 4.5, 5.5, and 4.5 $^\circ\text{C}$, respectively, above their bulk freezing temperatures. Figure 1 shows the temperature dependence of the surface tension γ of the F_8H_8 (dots). The formation of the SF layer at $T_s \approx 22 \text{ }^\circ\text{C}$ is indicated by a sharp change in the slope from a negative ($T > T_s$) to a positive ($T < T_s$) value. This is due to the fact that the surface tension's slope equals the difference in entropy per molecule in the bulk and at the surface. For a liquid surface the molecular entropy is higher than that of the bulk, and the slope is negative. However, when the surface crystallizes, the surface entropy is reduced below that of the liquid bulk,

and the slope becomes positive.^{1,4} The sharp slope change demonstrates that the transition is first order, as appropriate for a freezing transition. The bulk freezing is shown by the sharp drop in the surface tension at $T_f \approx 17.5 \text{ }^\circ\text{C}$.

Figure 1 also shows (line) the X-ray reflectivity at a fixed vertical momentum transfer of $q_z = 0.23 \text{ \AA}^{-1}$ ($q_z = (4\pi/\lambda) \sin(\alpha)$, where α is the grazing angle of incidence) as a function of temperature. The formation of the SF monolayer is indicated by a sharp jump in the intensity. Bulk freezing breaks up the smooth and flat surface, causing a sharp drop in the reflected intensity at T_f . The bulk (T_f) and surface (T_s) freezing temperatures in the surface tension and reflectivity scans, and thus also the SF range of existence, are seen to coincide, once the 0.5 $^\circ\text{C}$ shift between the thermistors of the two experimental cells are corrected for, as done in Figure 1. Both curves show no deviations from linearity, in particular no jumps between T_s and T_f , indicating that no further surface phase transitions occur in this region. In particular, no growth occurs in the thickness of the SF layer, which remains one molecule thick from its formation at T_s down to bulk freezing at T_f . In terms of a wetting transition, the formation of the SF layer at the free surface can therefore be classified as an incomplete wetting of the liquid by a crystalline monolayer.^{26,27}

As discussed above, in this low n/m range the SF layer is expected to be crystalline. Indeed a single GID peak is found for all three samples at $q_{\parallel} \approx 1.3 \text{ \AA}^{-1}$ ($q_{\parallel} = (4\pi/\lambda) \sin(2\theta/2)$, where 2θ is the diffraction angle) indicating an hexagonal in-plane packing of the molecules in the SF monolayer. A typical BR at the peak position of F_8H_8 is shown in Figure 2. Its contour plot is given under the measured BR. The general shape, elongated along the q_z direction at a fixed q_{\parallel} , as also observed in the contour plot, clearly indicates that the diffraction peak originates in a quasi-2D structure, i.e., an ordered monolayer. Moreover, as the peak of the BR is seen to be at $q_z \approx 0 \text{ \AA}^{-1}$, the

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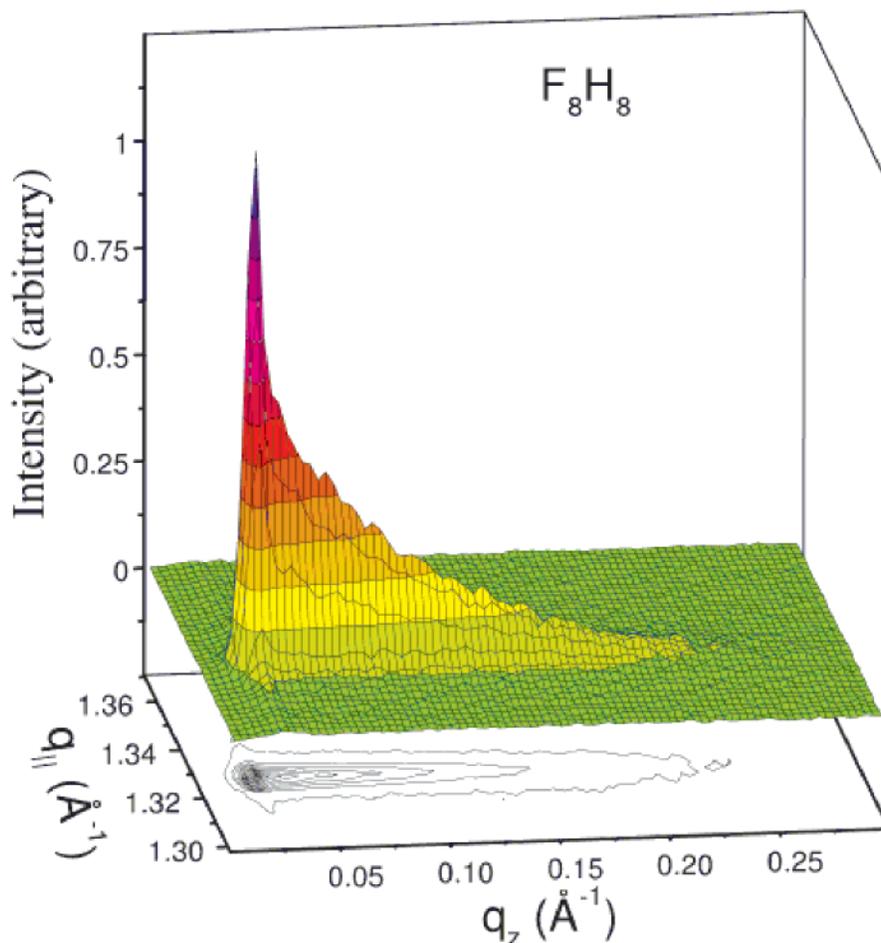


Figure 2. Bragg rod measured for the surface-frozen monolayer of F_8H_8 . A contour plot of the intensities is shown below the Bragg rod. The sharp peak close to $q_z = 0 \text{ \AA}^{-1}$ is the surface enhancement peak ("Vineyard peak") at the critical momentum transfer $q_x \approx 0.02 \text{ \AA}^{-1}$.

molecules of the crystalline monolayer must be aligned normal to the surface, as indeed expected for these molecules.^{12,15} The measured width of the BR at its base, Δq_z , is related to the apparent molecular length d through⁴ $(\Delta q_z d) = \pi$. This yields an apparent length of 23.9 Å, close to the extended length of the full molecule ($\sim 22.8 \text{ \AA}$), indicating that the H block of the molecule is not molten and takes part in the in-plane order. A fit to the measured BR profile of a simplified model, assuming a uniform effective cross section for the whole molecule, agrees well with the data and the values listed here. So does a more sophisticated model, which takes into account the different axis-normal form factors²⁸ due to the different cross sections of the two blocks.¹⁶

Integration over the intensity in the q_z direction at each q_{\parallel} yields the total scattered intensity vs q_{\parallel} , i.e., the GID scan. Such scans are shown in Figure 3 for $F_{10}H_8$ at two different temperatures, along with a fit to a Gaussian. The widths of the peaks are resolution limited, so that no systematic changes with temperature can be identified in the full width at half-maximum values. A lower bound for the coherence length is obtained from the measured diffraction peak widths as $\Delta q_{\parallel} \approx 0.005 \text{ \AA}^{-1}$. This implies that the ordered domains are at least 1000 Å across. A previous study of normal alkanes, performed with higher resolution,²² yields a 7-fold higher lower limit for the crystalline coherence length. For non-resolution-limited

lines, shape analysis should allow, in principle, distinguishing between quasi-long-range and true long-range order. The former results in algebraically decaying tails for the GID peak, while the latter should yield exponentially decaying tails.^{22,24,25} Unfortunately, our resolution was not high enough to support such an analysis.

The in-plane peak positions observed here correspond to a nearest-neighbor separation in the surface plane of $d = 2\pi/[q_{\parallel} \cos(30^\circ)] \approx 5.5 \text{ \AA}$. The values of d for the different SFA and temperatures are shown in Figure 4. The inset shows the $F_{10}H_8$ results on a magnified scale. The nearest-neighbor separation of each material is found to vary linearly with temperature. The slope of this variation yields a linear expansion coefficient of $(d/dT)/d = (6.3 \pm 0.3) \times 10^{-4}$, $(7.7 \pm 1.7) \times 10^{-4}$, and $(7.7 \pm 0.2) \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ for $F_{10}H_6$, F_8H_8 , and $F_{10}H_8$, respectively. These values are close to the $(9 \pm 0.5) \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ obtained in the high-resolution study²² of the fully protonated C_{20} -alkane SF mono. It is also close to the value of $6.5 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ obtained recently for the SF layer of the fully protonated C_{23} -alkane at the free surface of C_{23}/C_{12} solutions.²³ These values may be compared to $6.5 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ published for the R_{H} bulk hexagonal rotator phase in normal alkanes and the in-plane direction-averaged $11.8 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ and $2.55 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ of the orthorhombic R_1 rotator and herringbone crystal phases, respectively.^{12,29} A much lower value of $1 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$ was found for the

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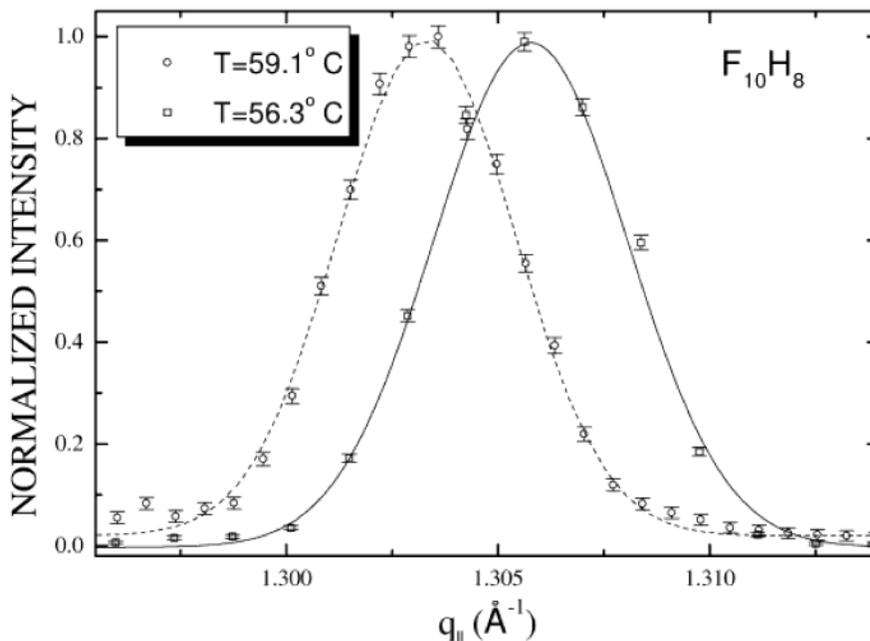


Figure 3. Grazing incidence diffraction peaks at the indicated temperatures for the surface-frozen monolayer of $F_{10}H_8$ (symbols). The shift between the peaks is due to the thermal expansion of the monolayer. The measured peaks are well fitted by Gaussian functions (lines).

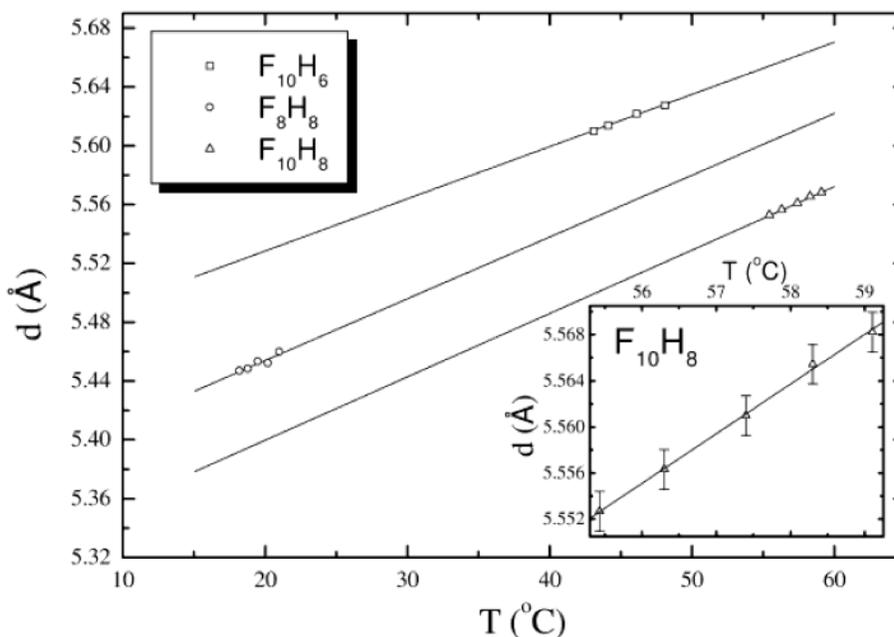


Figure 4. The nearest-neighbor distances calculated from the GID peak positions (symbols) and their fits by straight lines. A magnified view is shown in the inset for $F_{10}H_8$. For a discussion see text.

bulk thermal expansion of the structurally related, though polymeric and fully fluorinated, poly(tetrafluoroethylene) (PTFE).³⁰

As Figure 4 clearly shows for the F_8H_8 and $F_{10}H_8$ molecules, an increase in the F-block length by 25% reduces the molecular separation (extrapolated, of course, to the same temperature) but retains the same coefficient of expansion. The reduced intermolecular distance reflects, most probably, the increased vdW attraction of the longer molecules. Alternatively, it could be due to the smaller importance of the larger CF_3 terminal group in determining the intermolecular distances as the length of the F

block, and hence the number of CF_2 groups, increases. Surprisingly, a 33% increase in H-block length from $F_{10}H_6$ to $F_{10}H_8$ not only decreases the intermolecular distance, similar to the increase in the F block lengths, but also *increases* the expansion coefficient. This “softer” crystallinity can be understood perhaps as a shift in the balance between the H–H and the F–F interactions, toward lowering of the latter’s dominance. Indeed, the transition from the in-plane ordered low n/m SF monolayer to the in-plane disordered high n/m SF monolayer has been attributed in a previous study^{12,15} to a similar, though much larger, shift, which results in a change in the dominance from that of the F–F to that of the H–H interactions.

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Finally, the area per molecule in the frozen surface layer is obtained from the X-ray measurements as $A = 8\pi^2/(\sqrt{3}q_l^2)$. As can be observed in Figure 4, for a fixed F₁₀ block, the area per molecule was found to vary from a measured 26.6 Å² for F₁₀H₈ at $T \approx 55$ °C to a measured 27.6 Å² for F₁₀H₆ at a lower $T \approx 48$ °C or 27.9 Å² if extrapolated to the same $T \approx 55$ °C. This variation and the 15% difference between the linear expansion coefficients of F₁₀H₆ and F₁₀H₈ demonstrate that the H-block also influences the 2D lattice, even though the F-block dominates the structure. We note that the limiting molecular area in Langmuir films of semifluorinated molecules on water was found to *increase* with the fluorinated block length from 28.8 Å² for F₈H₁₆ to 34.4 Å² for F₁₂H₁₆ at $T \approx 25$ °C. By contrast, the extrapolated d values for F₈H₈ and F₁₀H₈ in Figure 4 at any given temperature show a *decrease* in d , and hence in the molecular area, with increasing fluorinated block length when the H block length remains unchanged. This may reflect fundamental differences in the molecular conformations and intermolecular interactions between surface-frozen and Langmuir monolayers, as also found for alkanes³¹ and alcohols.⁵ However, the structure of the surface-frozen monolayer was shown¹⁵ to undergo a

fundamental change with the H block's length at $n = 16$ from in-plane crystalline for $n < 16$ to in-plane smectic-like for $n > 16$. Thus, it is also possible that the different variation of the molecular area with m and n found here and in Langmuir films¹⁷ is due to the different H block regimes studied. Future studies over a wider range, and different combinations, of n and m may elucidate more accurately the role of the H-block in the formation and structure of the SF monolayer in SFAs and, in particular, in determining their thermal properties such as the thermal expansion.

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